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(54) IMPROVED CATALYSTS AND PROCESS FOR THE POLYMERIZATION AND COPOLYMERIZATION OF OLEFINS

(71) We, SOLVAY ET CIE, a body corporate organised under the Laws of Belgium, of 33, Rue du Prince Albert, Brussels 5, Belgium, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention relates to improved catalysts and process for the low-pressure polymerization and copolymerization of olefins.

In British Patent No. 1,140,649, dated October 17, 1967 in the name of the Applicants, several processes for the low-pressure polymerization of olefins in the presence of solid catalysts are described. These catalysts are prepared by reacting a solid compound of a bivalent metal M containing M—O bonds with a halogenated derivative of a transition metal. They are activated by means of an organometallic compound. Applied to the polymerization of ethylene, they show an exceptionally high activity and enable one to prepare polyethylenes which are characterized by a high linearity and adjustable melt indices in a broad range.

The main British Patent Specification No. 1,256,851 (Application 662/70), dated January 6, 1970, relates to catalysts for the low-pressure polymerization and copolymerization of olefins, comprising:

- a) an organometallic compound, or an organosilicon compound having at least one Si-H bond, and
- b) a solid product obtained by reacting a substantially anhydrous support consisting of a solid bivalent-metal compound with an organometallic compound, or with an organosilicon compound having at least one Si-H bond, this being either identical to or different from "a", separating the solid product resulting from the reaction, reacting this product with a halogenated de-

rivative of a transition metal, and separating the final solid reaction product; the molar ratio of "a" to the transition metal chemically bonded to the support being at least 2.

According to this Patent Application, the second constituent of the catalysts according to the invention is obtained by treatment of a solid support and is solid itself.

The solid support is a bivalent metal compound. It is preferably chosen among the compounds of calcium, zinc, manganese, cobalt or nickel and magnesium, magnesium being preferred. Mixed compounds of two or more bivalent metals may also be used. Among the compounds which are suitable as a solid support may be mentioned: the hydroxychlorides and other hydroxy halides, simple or complex oxides, complex hydroxides, alcoholates and salts of inorganic acids (sulfates, nitrates, phosphates or silicates for instance). Salts of organic mono- or polycarboxylic acids are also suitable.

The impregnation agent is an organometallic compound chosen among the organic derivatives of metals of groups I, II, III or IV of the Periodic Table and more particularly among the organometallic halides and organometallic hydrides, as well as the completely alkylated derivatives of these metals. Trialkylaluminiums are also used preferably but dialkylaluminium halides, alkylmagnesium halides, alkylaluminium hydrides, alkyltin hydrides and organometallic compounds of silicon having at least one Si-H bond may also be used.

It has now been found that when the solid support is an alcoholate of a bivalent metal and particularly a magnesium alcoholate, or any other compound of formula $X_{2-n}M(OR)_n$, where M is a bivalent metal, X is a monovalent inorganic radical, R is a monovalent hydrocarbon radical and n is a number so

that $0 < n \leq 2$, and when the impregnation agent is an alkylaluminum halide having a certain formula, given below, catalysts are obtained which show particular properties, including a further improved activity.

The present invention relates to improved catalysts for the low-pressure polymerization and copolymerization of olefins comprising:

a) an organometallic compound or an organosilicon compound having at least one Si-H bond; and

b) a solid obtained by reacting a substantially anhydrous support constituted by a solid bivalent metal compound with an organometallic compound identical to or different from the preceding one ("a"), separating the solid reaction product, reacting this product with a halogenated derivative of a transition metal and separating the solid reaction product, the molar ratio of "a" to the transition metal chemically bonded to the support being at least 2, wherein the solid bivalent metal compound is constituted by a compound of formula $X_{2-n}M(OR)_n$ where M is a bivalent metal, X is a monovalent inorganic radical, R is a monovalent hydrocarbon radical containing from 1 to 20 carbon atoms and n is chosen so that $0 < n \leq 2$, and the organometallic compound which is reacted with it is an alkylaluminum halide having the formula AlR_pY_{3-p} , where Y is a halogen atom, R' is an alkyl radical containing from 1 to 20 carbon atoms and p is at least 1 but less than 2.

The catalysts of the invention can be used for the polymerization and the copolymerization of olefins containing from 1 to 6 carbon atoms and in particular for the preparation of polyethylene, polypropylene and ethylene-propylene copolymers.

The polymerization and copolymerization may be carried out according to known methods: in the gaseous phase, i.e. in the absence of any liquid medium, or in the presence of a dispersing agent in which the monomer is soluble. Suitable dispersing agents are inert hydrocarbons, which are liquid under the polymerization conditions, or the monomers themselves maintained in the liquid state under their saturated vapour pressure.

Depending on the temperature at which the polymerization is carried out and the nature of the polymerization medium, the polymer is dissolved in the polymerization medium or dispersed in it in the form of solid particles.

The dispersion process is particularly economic as it enables one to operate at a lower temperature and to recover well shaped polymer particles.

The catalysts according to the invention comprise two constituents. The first of these constituents is preferably an organometallic compound chosen among the organic derivatives of metals of groups I, II, III and IV

of the Periodic Table. Organometallic halides and hydrides, as well as completely alkylated derivatives of these metals may be used. Examples of these are dialkylaluminum halides, alkylmagnesium halides, alkylaluminum hydrides and alkyltin hydrides. Use may also be made of organosilicon compounds having at least one Si-H bond. Trialkylaluminums, however, are preferred.

The quantity of organometallic compound as a first catalyst constituent to be used during polymerization is not critical. However, there must be a molar excess of this first constituent in the polymerization medium with respect to the quantity of transition metal which is chemically bound to the solid support. The molar ratio of these two quantities is preferably comprised between 10 and 200.

This solid bivalent metal compound has the general formula $X_{2-n}M(OR)_n$ in which:

—M is a bivalent metal preferably selected among calcium, zinc, manganese, cobalt or nickel, and more preferably magnesium

—X is a monovalent inorganic radical preferably selected among halide radicals, i.e. chloride, bromide, iodide or fluoride

—R is a saturated or unsaturated monovalent hydrocarbon radical comprising from 1 to 20 and preferably from 1 to 10 carbon atoms selected among branched or non branched alkyl radicals, optionally substituted cycloalkyl radicals, aryl, arylalkyl and alkylaryl radicals,

—n is a number greater than 0 and lower than or equal to 2; it is not at all necessary that n is an integer because non-stoichiometric compounds are suitable for the realization of the invention.

Examples of compounds which may be used for the preparation of the new polymerization catalysts according to the invention are:

—magnesium, calcium, zinc, manganese, cobalt and nickel alcoholates and phenolates

—alkoxy- and phenoxymagnesium halides and similar derivatives of the other bivalent metals mentioned above

—reaction products and intimate mixtures of alcoholates and/or phenolates of bivalent metals with halides of the same metals

—mixtures and combinations of two or more compounds above mentioned.

It is well understood that the terms phenoxy and phenolate must be taken in their general meaning and that, as well as covering the derivatives of the benzenic series, they extend also to the corresponding polycyclic derivatives, for example to derivatives of naphthalene, phenanthrene, anthracene, etc.

Before any reaction, the solid compounds are treated in order to dry them as completely as possible.

It is indeed essential that the solid compounds be as dry as possible before being processed, because the alkylaluminum halide reacts with water.

The granulometry of the solid compound is not critical. It is, however, chosen relatively coarse, in order to avoid obstruction due to too fine support particles.

5 The alkylaluminium halide used for the first reaction is a compound of formula $AlR_p'Y_{3-p}$, where Y is a halide radical such as chloride, fluoride, bromide or iodide, p is at least 1 but less than 2, and need not be an integer because it only indicates the average composition of the reactant, which may be a mixture of more than one alkylaluminium halide, and R' is an alkyl radical containing from 1 to 20 and preferably from 10 15 1 to 10 carbon atoms.

Ethylaluminium dichloride, ethylaluminium sesquichloride, n-butyl-aluminium dichloride and n-octylaluminium dichloride are particularly useful.

20 For its first reaction the solid compound may be suspended in a diluent which is inert towards organometallic compounds. An alkane or cycloalkane (hexane or cyclohexane for instance) is generally chosen as diluent. The treatment is preferably carried out under a flow of inert gas such as nitrogen in a closed container which is agitated during the whole duration of impregnation.

30 To the suspension of solid compound in the diluent, the alkylaluminium halide is added as such or dissolved in a solvent. This solvent may be identical to the diluent which is used to suspend the support.

35 The duration of the reaction may have a certain influence on the performances of the catalyst. It is generally between 5 and 240 minutes, preferably between 10 and 60 minutes. In most cases, a duration of thirty minutes seems to be sufficient. For the whole duration of the reaction, the suspension of solid compound is maintained at a temperature between room and boiling temperature of the diluent under normal pressure. Preferably, the temperature is maintained between 40 45 20 and 140° C.

50 The transformation of the solid is often accompanied by an exothermal phenomenon which occurs after a lapse of time which varies depending on the reaction conditions. On account of the existence of this phenomenon, the reactions are carried out under vigorous agitation.

55 The reaction is accompanied by a very important transformation of the solid compound: it is namely observed that its specific surface, when it is initially low e.g. lower than 10 m²/g, passes over, after reaction, to several times its initial value, e.g. more than 40 m²/g and preferably more than 100 m²/g.

60 From the chemical point of view, the reaction comprises an at least partial exchange of alkoxy or phenoxy radicals and halogen between the bivalent metal and aluminium and is accompanied by the fixation of a certain

quantity of this latter metal in a chemically combined form. 65

The magnitude of the exchange and the quantity of fixed aluminium are influenced by the nature and the quantity of alkylaluminium halide used for the impregnation. An excess of alkylaluminium halide causes a more thorough exchange which may even be practically total if the reaction conditions are sufficiently strong. 70

At the end of the reaction time, the agitation is stopped and the solid product from the first reaction is separated, for example by filtration. The product is then washed by means of an inert solvent in order to eliminate the reactant in excess. 75 80

In the second stage of the preparation of the second catalyst constituent the solid product is treated by means of a halogenated transition metal compound. This treatment is preferably carried out in the absence of any diluent, in suspension in the halogenated transition metal derivative maintained in the liquid state at the temperature used. This temperature is usually between 40 and 180° C. The treatment is carried out in the absence of moisture. It is generally performed for about one hour, then the treated product is washed by means of an inert diluent in order to eliminate the excess of halogenated transition metal derivative which has not been fixed on the support. It may then be dried for example in a flow of inert gas. In this way the second polymerization catalyst constituent is obtained. 85 90 95

The halogenated transition metal compound used for the treatment of the solid product is preferably one of the following chlorides, bromides, alkoxyhalides and oxyhalides of metals of groups IV, Va and VIa of the Periodic Table. We particularly prefer to use the chlorinated derivatives of titanium and of vanadium (TiCl₄, VCl₃ or VOCl₃ for example). The best results are obtained with TiCl₄. 100 105

After the reaction with the alkylaluminium halide and after treatment with a halogenated transition metal derivative, the solid compound, the alkylaluminium halide and the halogenated derivative are chemically bound in an activated complex. None of these components of the activated complex can be separated by physical means such as by washing with solvents. 110 115

The activated complex, i.e. the second catalyst constituent, may be contacted with the first catalyst constituent in the polymerization vessel or before its introduction into the polymerization vessel. It may then be matured by contact with the first catalyst constituent at room temperature or above. 120

The catalysts according to the invention show a very high activity. Hence, the catalytic residues are in such a low concentration with respect to the polymer that their presence is not harmful for any application. Con- 125

sequently it is superfluous to purify the polymers prepared according to the process of the invention.

The polyolefins prepared with the catalysts according to the present invention show remarkable properties. They are characterized namely by a high molecular weight. So, the polyethylenes obtained with the catalysts of the invention have a melt index (Norm ASTM D1505—57T) which is generally lower than 1 g/10 min, even when the polymerization is carried out at a relatively high temperature and in the presence of hydrogen.

The catalysts prepared from products of the first reaction containing a high proportion of halogen are specially suitable for the preparation of polyolefins with a high molecular weight. To prepare these polyolefins it is preferred to start from products of the first reaction, the halogen/metal M atomic ratio of which is higher than 1.5. The best results are obtained when this ratio is higher than 1.7.

The polyolefins with a high molecular weight have a considerable technical importance, because they are preferably used in applications where the polymer is extruded, as for example for the manufacture of elongated material of uniform cross-section, or bottles (by blow moulding).

Example 1

10 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ are introduced into 20 ml of a solution containing 165.5 g of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, per 100 g of hexane, which corresponds to an atomic ratio Cl/Mg of 1.5.

The mixture is maintained at 25° C. for 1 hour. After separation and drying of the reaction product, a solid compound is recovered. The elementary analysis of this compound shows that it contains 209 g of Mg and 19 g of Al per kg.

Its specific surface is 250 m²/g whereas that of the starting magnesium ethylate was lower than 10 m²/g. This shows the importance of the transformation undergone.

The product of this first reaction is treated

by means of TiCl_4 for 1 hour at 140° C. It is then washed until elimination of any trace of chloride in the washing solvent, then dried under a flow of dry nitrogen.

Then analysis of the catalytic solid thus obtained indicates the following composition:

Mg: 197 g/kg	Cl: 678 g/kg
Al: 7.6 g/kg	Ti: 49 g/kg

11 mg of this solid are introduced in a 1.5 l autoclave containing 0.5 l of hexane and 200 mg of $\text{Al}(\text{i.C}_4\text{H}_9)_3$. The polymerization is then carried out at 85° C. for 1 hour under ethylene and hydrogen pressures. The pressures of ethylene and hydrogen are respectively equal to 10 and 4 kg/cm². The pressure is maintained constant by continuous introduction of ethylene.

178 g of polyethylene are obtained, which corresponds to a specific activity of 33,000 g PE/h.g.Ti.atmC₂H₄ and to a catalytic productivity of 1620 g PE/h.g solid.atmC₂H₄.

The polyethylene obtained is characterized by a melt index (measured according to norm ASTM D 1505—57T) of 2.59 g/10 min.

Examples 2 to 7

A series of catalytic solids are prepared as in example 1, but starting from variable quantities of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. The data concerning the preparation of the catalysts and the polymerization runs are given in Table I.

In examples 2, 4 and 6, the first reaction is carried out at 70° C. instead of 25° C.

Examples 2 to 7 show that the products of the first reaction, which are characterized by a high Cl/Mg atomic ratio, lead to polymers with a low melt index and consequently with a high molecular weight.

Examples 6 and 7 show that the first reaction may give rise to the formation of a product which is practically free from alkoxide groups. The Cl/Mg atomic ratio is higher than 2, because part of the chlorine has been fixed on the aluminium.

TABLE I

	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
<u>1st Reaction</u>						
Cl/Mg atomic ratio in the reaction medium	0.38	1.56	2.5	3.6	5	5
Analysis of product: Mg g/kg	215	207	203	184	231	177
Al g/kg	5	17	26	21	20	32
Cl g/kg	38	182	339	446	703	570
Cl/Mg atomic ratio in the product	0.12	0.60	1.14	1.66	2.08	2.20
<u>2nd Reaction</u>						
Analysis of product: Mg g/kg	221	188	170	159	176	167
Al g/kg	18	11	8.5	9.5	23	23
Cl g/kg	680	669	682	609	699	679
Ti g/kg	40	61	70	57	58	58
<u>Polymerization</u>						
Quantity of catalytic solid mg	11	4	5	5	7	7
Quantity of polyethylene produced g	151	137	96	120	68	96
Melt index of PE g/10 min	0.65	1.01	0.62	0.24	0.14	0.09
Catalytic activity g PE/h.g Ti.atm C ₂ H ₄	34,000	56,000	27,400	42,000	16,700	23,600
Catalytic productivity g PE/h.g solid.atm C ₂ H ₄	1,370	3,425	1,920	2,400	970	1,370

Examples 8 to 11
With the catalytic solid of example 3, a series of polymerization runs was realized with

activators having a diverse nature. The results of these runs are given in Table II below.

5

TABLE II

	Ex. 8	Ex. 9	Ex. 10	Ex. 11
Nature of activator	$\text{Al}(\text{CH}_3)_3$	$\text{Al}(\text{iC}_8\text{H}_{17})_3$	isoprenyl Al (*)	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$
Quantity of activator millimoles	1	1	1	1.6
Quantity of solid catal. mg	6	7	11	12
Quantity of PE produced g	112	147	168	209
Melt index of PE g/10 min	0.45	1.76	0.89	0.53(**)
Catal. activity g.PE/h.g Ti. atm C_2H_4	7,400	34,500	22,000	28,500
Catal. productivity g.PE/h.g solid cat. atm C_2H_4	112	2,100	1,530	1,740

(*) Reaction product of isoprene with triisobutylaluminium.

(**) High load melt index.

It is relevant to point out that the new catalysts may be used with a large variety of activators and may give rise to polyethylenes having a broad range of molecular weights.

Example 12

20 g of magnesium ethylate $\text{Mg}(\text{OC}_2\text{H}_5)_2$ are introduced into 100 g of a solution containing 50% by weight of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ in hexane. The reaction is then carried out as described in Example 1.

The magnesium ethylate which has reacted with $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ is then treated by means of VOCl_3 which is heated under reflux for 1 hour.

After washing and drying as in example 1, the solid product obtained contains 142 g of magnesium, 15 g of aluminium, 607 g of chlorine and 132 g of vanadium per kg.

A polymerization run is carried out which is the same as in example 1, except that 21 mg of the solid product are used.

14 g of polyethylene are obtained, which corresponds to a specific activity of 470 g of polyethylene/h.g. V.kg/cm² C_2H_4 . The melt index of this polyethylene is 1.03 g/10 min.

Example 13

20 g of magnesium phenate $\text{Mg}(\text{OC}_6\text{H}_5)_2$ are introduced into 50 ml of hexane, then 72 ml of a 415 g/l $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ solution in hexane are added under agitation. The suspension is heated under reflux (at about 70° C.) for 1 hour.

After separation and washing with hexane

at 70° C., a solid product is recovered. The elementary analysis of this solid shows that it contains 192 g of Mg, 36 g of Al and 493 g of Cl per kg.

The Cl/Mg atomic ratio is thus 1.75.

This solid is then reacted under the conditions given in Example 1. There is obtained a catalytic solid having the following composition:

Mg: 179 g/kg Cl: 668 g/kg
Al: 32 g/kg Ti: 50 g/kg

A polymerization test is carried out under the conditions set forth in Example 1, except that 7 mg of catalytic solid are used.

There are obtained 103 g of polyethylene, which corresponds to a catalytic activity of 29,400 g PE/h.g.Ti.atm C_2H_4 , and to a productivity of 1470 g.PE/h.g solid.atm C_2H_4 .

The polyethylene obtained is characterized by a melt index of 0.58 g/10 min.

WHAT WE CLAIM IS:—

1. A catalyst for the low pressure polymerization or copolymerization of an olefin or olefins, comprising:

a) an organometallic compound or an organo-silicon compound having at least one Si-H bond; and

b) a solid obtained by reacting a substantially anhydrous support constituted by a solid compound of a bivalent metal with an organometallic compound which is identical

- to or different from compound "a", separating the solid reaction product, reacting this product with a halogenated transition metal compound and separating the solid reaction product, the molar ratio of "a" to the transition metal chemically bonded to the support being at least 2, wherein the solid compound of a bivalent metal is constituted by a compound of formula $X_{2-n}M(OR)_n$ where M is a bivalent metal, X is a monovalent inorganic radical, R is a monovalent hydrocarbon radical containing from 1 to 20 carbon atoms, and n is a number greater than 0 but not greater than 2, and the organometallic compound with which this compound is reacted is an alkyl-aluminium halide having the formula AlR'_pY_{3-p} , where Y is a halogen atom, R' is an alkyl radical containing from 1 to 20 carbon atoms and p is at least 1 but less than 2.
2. A catalyst according to claim 1 wherein compound "a" is an organic derivative of a metal of group I, II, III or IV of the Periodic Classification of the Elements.
3. A catalyst according to claim 2 wherein compound "a" is an alkylated derivative of aluminium.
4. A catalyst according to claim 1, 2 or 3, wherein the solid compound of a bivalent metal comprises a compound of calcium, zinc, magnesium, cobalt, nickel or manganese; and is an alcoholate or phenolate or an alkoxyhalide or phenoxyhalide of one of these

metals, or comprises a reaction product or intimate mixture of an alcoholate or phenolate of one of these metals with a halide of one of these metals, or any other mixture or combination of two or more of these compounds.

5. A catalyst according to claim 1, 2, 3 or 4, wherein the halogenated transition metal compound is a chloride, bromide, alkoxyhalide or oxyhalide of a metal of group IVa, Va or VIa of the Periodic Classification of the Elements.

6. A catalyst according to claim 1, substantially as described in any of the foregoing examples.

7. A process for the low pressure polymerization or copolymerization of an olefin or olefins, wherein a catalyst according to any of claims 1 to 6 is used.

8. A process for the low pressure polymerization of ethylene, wherein a catalyst according to any of claims 1 to 6 is used.

9. A process according to claim 7 substantially as described in any of the foregoing Examples.

10. An olefin polymer or copolymer obtained by means of a catalyst according to any of claims 1 to 6 or a process according to claim 7, 8 or 9.

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